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Carrier-density dependence of the hole mobility in doped and undoped regioregular poly(3-hexylthiophene)

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We investigate the mobility of poly(3-hexylthiophene) (P3HT) over a carrier-density range from 10^{15} to $10^{20}\,cm^{-3}$. Hole-only diodes were used for densities below $10^{16}\,cm^{-3}$ and field-effect transistors were used for carrier densities higher than $10^{18}\,cm^{-3}$. To fill the gap, intermediate densities were probed using chemically doped Schottky diodes and transistors. Combining of the mobilities in doped and undoped devices experimentally establishes the full relation of the mobility over the whole carrier-density range.

1 Introduction Solution-processable conjugated polymers such as polythiophene derivatives are attractive candidates for application in low-cost and flexible microelectronic devices. The electrical transport is dominated by thermally assisted intermolecular hopping of the charge carriers in a Gaussian density of states (DOS). The transport depends on carrier density, temperature, and electric field [1–6]. At room temperature and at relatively small electric field the transport is dominated by the carrier-density and the field dependence plays a negligible role [6, 7]. Experimentally capturing the full extent of the relation between mobility and carrier density is necessary for understanding and improving the device performance. For poly(*p*-phenylene vinylene) derivatives the mobility extracted from diodes is low, around $10^{-7}\,cm^2/Vs$, and independent of carrier density. The mobility extracted from field-effect transistors however increases with charge carrier density up to typically $0.001\,cm^2/Vs$. The difference originates from the charge carrier density, which in diodes is typically 10^{15}–$10^{16}\,cm^{-3}$ and in transistors from 10^{18} to $10^{20}\,cm^{-3}$ [8]. However, a full mobility carrier-density relation is hindered by a gap in the carrier density between 10^{16} and $10^{18}\,cm^{-3}$ [8, 9].

Polythiophenes have been extensively applied in field-effect transistors (FET) [10, 11] and solar cells [12]. The benchmark is regioregular poly(3-hexylethiophene) (rr-P3HT). To probe the mobility in the gap of 10^{16}–$10^{18}\,cm^{-3}$, we deliberately doped rr-P3HT [13]. Doping in organic semiconductors has been an important topic since the introduction of these semiconductors [14, 15]. More recently achievements have been made in the field of stable n-type doping and solution-processed doping [16–18]. In this work we investigated hole-only diodes (doped), Schottky diodes, and (doped) transistors. In this way over the whole range of charge carrier densities, the mobility can be unified by a zero-field mobility with a density dependent term based on hopping in an exponential density of states (DOS) [8, 19].

2 Experimental methods Regioregular poly(3-hexylthiophene) (P3HT) was obtained from Imperial College London and used without further purification. The molecular weight was 33,000 g/mol as measured by GPC and the regioregularity was >97%, as measured by NMR. The polymer was spincoated from chloroform, 20 mg/ml, yielding films with a thickness between 100 and 200 nm. Hole-only diodes were fabricated on glass substrates with a patterned layer of ITO. A 60 nm thin layer of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic acid) (PEDOT:PSS) was spin-coated on top of the ITO as Ohmic anode. The mobile ions in PEDOT:PSS however hamper reliable capacitance–voltage (*C*–*V*) measurements. Hence Schottky diodes were fabricated with a Au anode. After spin-coating rr-P3HT, all diodes were annealed at 150 °C for 2 h in vacuum. Hole-only diodes were finished by evaporating an electron blocking contact of 20 nm Pd and 80 nm Au. Schottky diodes were finished by evaporating a cathode of 90 nm Al. Current–voltage characteristics of the diodes were recorded in the dark and in nitrogen atmosphere using a Keithley 2400 SourceMeter. *C*–*V* measurements of Schottky diodes were conducted with a Solartron SI 1260 impedance/gain-phase analyzer.

Field-effect transistor substrates were fabricated on n^{++}-Si monitor wafers that act as a common gate. A 200 nm thermally grown oxide layer passivated with hexamethyldisilazane was used as gate dielectric. Au source and drain electrodes with a thickness of 100 nm were lithographically defined using a 10 nm Ti adhesion layer. The semiconductor rr-P3HT was spin-coated and annealed as described above. Transfer and output characteristics were recorded in vacuum and in the dark using a Keithley 4200 SCS semiconductor characterization system.

To chemically dope rr-P3HT, we exposed the devices to vaporized trichloro-(1H, 1H, 2H, 2H)-perfluorooctylsilane (TCFOS; Sigma–Aldrich) at a partial pressure of 2×10^{-1} mbar. The transfer characteristics of the transistors were measured as a function of exposure time [20]. We note that in the case of Schottky diodes the evaporation of the top electrode was performed after the doping process to guarantee a uniformly doped semiconductor.

3 Results and discussion

The current density of a rr-P3HT hole-only diode as a function of applied voltage is presented in Fig. 1a. The transport was measured as a function of temperature. At low bias the current density scales with the voltage squared, indicating space-charge-limited current (SCLC) with a constant mobility. PEDOT:PSS is an Ohmic contact to rr-P3HT, because the work function matches the energy of the highest occupied molecular orbital (HOMO) of rr-P3HT [21]. The transport in the diode is then bulk limited. At high bias the current density is enhanced. Charge transport is due to thermally activated hopping between localized states at the Fermi level. Device simulations were performed by using a numerical drift-diffusion model [22], incorporating a hopping mobility that depends on both charge-carrier density and electric field [12, 23]. Figure 1a shows that for all temperatures a perfect agreement between measured and calculated current densities is obtained. As fit parameters we used a room temperature zero-field mobility of $1.5 \times 10^{-4}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ with an activation energy of about 0.2 eV, a zero-field conductivity of $5 \times 10^6\,\mathrm{S\,m^{-1}}$, a characteristic temperature for the exponential DOS, T_0, of 475 K and an overlap parameter α^{-1} of 3 Å. The numbers agree well with reported values for rr-P3HT [8]. We note that at room temperature and for the low applied bias the density dependence dominates and the electric field dependence is negligible. To extract from the fit the charge-carrier density *versus* mobility relation we used the procedure reported by Craciun et al. [9]. The mobility is presented later as a function of average charge density in Fig. 3.

In order to increase the charge-carrier density we fabricated doped Schottky diodes. As a reference however, first undoped diodes were investigated. The Schottky diodes exhibit a rectification of more than six orders of magnitude. The current in forward bias is presented in Fig. 1b. The current density is calculated with the same numerical model as for the hole-only diodes using identical fit parameters. The solid line in Fig. 1b shows that a good agreement between calculated and measured current densities is obtained. After the undoped Schottky diodes were characterized, the diodes were doped. Exposing rr-P3HT to vaporized TCFOS yields p-type doping with additional mobile holes [13, 20]. Figure 1b shows that the current density in forward bias increases. The origin is an increase in mobility due to an increased charge density. To quantify the relation we determined the charge-carrier density independently from *C*–*V* measurements in reverse bias. We followed a literature procedure as presented previously in Ref. [18]. An AC voltage of 100 mV was superimposed to the applied reverse DC bias and a frequency scan was made from 10 Hz to 20 MHz at each bias. By modeling the diode as a parallel RC circuit for the depletion region in series with another RC

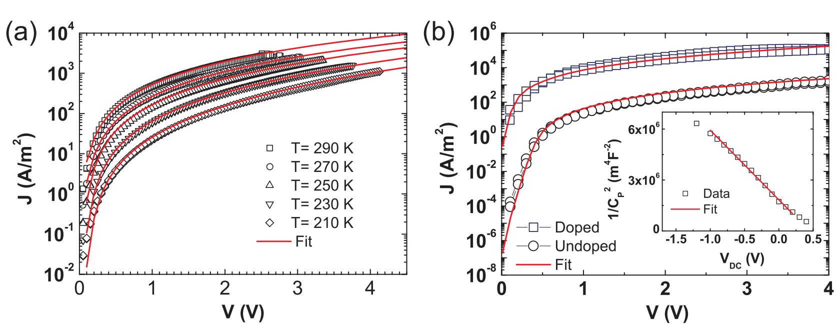

Figure 1 (online color at: www.pss-b.com) (a) Current density *versus* applied bias for a rr-P3HT hole-only diode with a thickness of 135 nm, measured as a function of temperature. The solid lines represent the fit according to the carrier-density-dependent and field-dependent mobility model. (b) Current density *versus* voltage of an undoped and a doped Schottky diode with a thickness of 195 nm. The solid lines represent the fit according to the model. The inset shows the inverse of the capacitance squared *versus* DC bias of the doped Schottky diode. The solid line represents the linear fit.

circuit for the semiconductor bulk, the capacitance of the depletion region, C_p, was extracted. The inset of Fig. 1b shows C_p^{-2} *versus* reverse bias for a diode exposed 20 min to TCFOS vapor. A straight line was obtained and the acceptor density N_a was calculated from the slope. The extracted value was then used as input to calculate the forward current density. The solid line in Fig. 1b shows that a good agreement is obtained. From the calculation the corresponding average mobility is extracted. For three doped Schottky diodes the mobility is presented as a function of charge-carrier density in Fig. 3.

To probe the mobility at high-carrier density field-effect transistors were investigated. The carrier density quadratically decreases with the distance from the semiconductor gate–dielectric interface. The density at the interface dominates the transport and was calculated as a function of gate bias as reported previously [24]. The linear mobility was approximated at each gate bias from:

$$\mu = \frac{L}{WC_i V_D}\frac{\partial I_D}{\partial V_G}$$

where all symbols have their usual meaning [25]. The extracted mobility *versus* carrier-density values for an undoped rr-P3HT transistor are presented in Fig. 3.

Exposing the transistors to TCFOS vapor leads to doping of rr-P3HT. The doping density can be varied by changing the exposure time. Transfer curves recorded *in situ* at different exposure times are presented in Fig. 2. A shoulder appears in the transfer curve; a higher positive bias is needed to deplete the doped bulk semiconductor and pinch-off the channel. Also the on-current at negative gate bias, in accumulation, slightly increases due to a shift in threshold voltage. The threshold voltage, defined as the on-set of the channel current at flat band [26], shifts to positive values upon doping. Each transfer curve in Fig. 2 is corrected for its

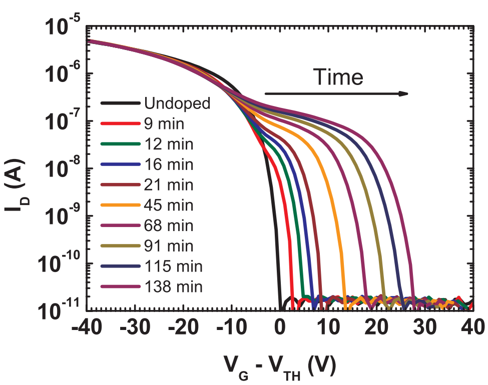

Figure 2 (online color at: www.pss-b.com) Transfer curves in the linear regime of a rr-P3HT field-effect transistor in vacuum before and after exposure to TCFOS vapor at room temperature for different exposure times. The channel length and width are 10 and 2500 μm, and the semiconductor thickness was 100 nm. The drain bias was −2 V and the transfer curves are corrected for the threshold voltage shift with respect to the pristine undoped transistor at $t = 0$ [20]. The threshold voltages range from 5.8 V for the undoped transistor to 19 V after 138 min.

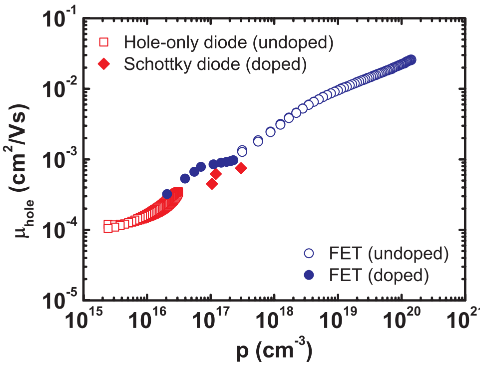

Figure 3 (online color at: www.pss-b.com) Charge carrier mobility *versus* carrier density of rr-P3HT as extracted from undoped hole-only diodes, doped Schottky diodes, and undoped and doped field-effect transistors.

threshold voltage indicating that the accumulation currents are identical within experimental error. The corrected transfer curves show a cross-over from an accumulation mode into a bulk depletion mode transistor [20, 27]. The current in accumulation is dominated by the channel current, while in depletion, at positive gate bias, the current is mainly flowing through the bulk semiconductor. The doping density can be calculated from the pinch-off voltage and the mobility can be calculated from the current at flat band conditions [20, 27]. The extracted mobilities and carrier densities are presented in Fig. 3 as well.

The extracted mobility and charge-carrier density values from all devices investigated are presented in Fig. 3. The gap between the undoped diodes and undoped transistors is probed with the doped diodes and the doped transistors. Moreover Fig. 3 shows that the hole mobility is flattening for charge carrier densities below 10^{16} cm^{-3} and increases with a power law for higher charge densities. The power law dependence is due to hopping transport in disordered semiconductors [12, 19]. Slight deviations from the power law at intermediate density might be due to anisotropy in the charge transport caused by the nanocrystalline nature of rr-P3HT.

4 Conclusion In summary, we have experimentally probed the charge carrier mobility as a function of carrier density for rr-P3HT over a wide density range. The mobility at low, 10^{15}–10^{16} cm^{-3}, and high, 10^{18}–10^{20} cm^{-3}, carrier density was extracted from undoped hole-only diodes and field-effect transistors, respectively. The room temperature mobility is nearly constant at densities below 10^{16} cm^{-3}, whereas the mobility increases with a power law for densities higher than 10^{18} cm^{-3}. The mobility at intermediate density has been probed by chemically doped Schottky diodes and transistors and unites the low- and high-density regimes.

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